INFLUENCE OF ALKENYL SUCCINIC ACID LUBRICATION ON WATER-REPELLENT TREATMENTS FOR LEATHER*

ABSTRACT

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Chrome side leather, retanned with glutaraldehyde, was lubricated with an alkenyl succinic acid by two dipping procedures. This substrate was then treated with three water-repellent agents, i.e. silicone, Scotchgard,‡ and Quilon, and the dynamic water-resistance of the leather evaluated. Lubrication with the alkenyl succinic acid seemed to improve the efficiency of the water-repellent treatments.

INTRODUCTION

The usual methods for fat-liquoring leather involve the use of oil-in-water emulsions which are obtained through the use of various types of surface-active agents, primarily sulfated oils. These agents generally impart a hydrophilic nature to the leather fiber and oppose the effect of water-repellent materials. It has been necessary to limit the amount of such oils for leathers to be treated with water-repellent materials (1). Thus lubrication plays an important role in preparing a leather substrate for water-repellent treatments.

Recently von Fuchs developed a novel approach to lubrication of leather that avoided use of sulfated oils and was recommended for lubrication of leather to which an alkenyl succinic acid (ASA) was subsequently applied as a water-repellent (2, 3, 4, 5). In this process the lubricant and the water-repellent chemical are the same material (i.e., an alkenyl succinic acid in which the average chain length in the alkenyl group is about 18 carbon atoms). von Fuchs, as well as later investigators (6, 7), have adequately studied this process using ASA for a dual purpose, i.e., as a leather lubricant, at which stage the leather is not water-resistant, and subsequently as a water-repellent material.

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‡Mention of brand or firm names does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.

The object of the present paper was to study the application of other types of water-repellent materials, such as silicones, Scotchgard, and Quilon, to leather that had been lubricated by the von Fuchs' process, as well as by a modified process involving a water-compatible system. Since materials generally used to impart water-resistance to leather are comparatively expensive, a desirable objective was to obtain a high degree of water-resistance with a relatively small amount of water-repellent chemical. In practice it is generally found that as much as ten percent by weight is required, which is considerably more than the amount required to coat the leather fiber completely with a thin film (8, 9).

EXPERIMENTAL

Materials.—The sides used in the following experiments were commercially tanned chrome grain splits, 5–6 oz., soaked back by drumming in water for 30 minutes and drained. The sides were retanned with five percent glutaraldehyde (25 percent solution) according to the recommended procedure (10). The sides were wrung at a tannery and contained about 60–65 percent water. The alkenyl succinic acid used in this study was Casyl 18, obtained from the Humphrey Wilkinson Corporation. The mineral spirits was a high flash point petroleum naphtha, boiling range 365 to 399°F., obtained from the American Mineral Spirits Company. The tetrahydrofurfuryl alcohol was obtained from the Quaker Oats Company. Dow Corning® Silicone 1109 resin; Fluorochemical FC-146 Scotchgard of Minnesota Mining & Manufacturing Company; and Quilon M of E. I. duPont Company were the water-repellents used.

Lubrication.—One side, labeled "Side M," was lubricated by the method described by von Fuchs (2). The wrung side (approximately 61 percent moisture) was pulled through a solution containing two percent by weight of Casyl 18 in mineral spirits. From the gain in weight on dipping and the concentration of ASA in the solution, the uptake of ASA was calculated to be 0.8 percent. The impregnated side was then toggle-dried under a slight tension and allowed to air-dry for one week. It was then returned to a tannery to be sammied and staked.

A second side, labeled "Side T," was lubricated by a somewhat modified procedure. The wet side, after wringing to approximately 62 percent moisture was pulled through a solution containing 1.5 percent of Casyl 18 in a 50–50 mixture of tetrahydrofurfuryl alcohol in water. This mixture was used since the solution would tolerate additional moisture without causing ASA to be precipitated. From the uptake of solution and its concentration, the deposition of ASA was calculated to be one percent. The impregnated side was crust-dried, sammied, and staked as described above for Side M.

Impregnation with Water-Repellent.—After staking, each side was marked off in 4″ x 4″ squares, stratified into three major areas: bend, flank and shoulder, as shown in Figures 1 and 2. The samples were labeled for identification purposes and cut out. Treatment with the water-repellent was carried out in groups. The groupings were determined by combining all the samples of a strata which were to receive a particular treatment, and then weighing them as a group before and after treatment. The time of treatment was visually determined by the "wetting" of the samples and the cessation of bubbling, but, at most, immersion time was of only a few minutes duration. Data on uptake are summarized in Table I.

The water-repellent treatments for each group were: A — Scotchgard; B — Quilon; C — low-level silicone; and D — high-level silicone. Each lot from bend, flank, and shoulder was impregnated separately.

In the silicone treatments the Dow Corning 1109 resin, a fifty percent solution of silicone in tetrachloroethylene (11), was diluted to solids contents of three and five percent. These two solutions were used to impregnate the leather specimens so as to obtain a high and a low level treatment. The pickup of silicone was 6.6 and 10.8 percent for Side M and 6.4 and 10.3 percent for Side T.

The treatment with Quilon M was effected as recommended by the manufacturer (12). The solution, 29–30 percent chrome complex, was diluted to 2.7 percent complex with water as directed under Method II in supplier's bulletin (12). The average uptake of chrome complex was calculated (as above) to be 5.5 percent for specimens from Side M and 5.2 percent for those from Side T.

Scotchgard FC-146, a 30 percent solution of active ingredient stated to be a chrome complex of a long-chain fluorochemical (13), was diluted with water to give a solution of 2.7 percent active ingredient. The leather specimens were immersed in this solution and the average pickup of Scotchgard was calculated to be 5.0 and 4.9 percent for Sides M and T respectively.

Evaluation of Water-Resistance (14, 15).—After impregnation of the leather specimens with the water-repellents, they were permitted to dry at ambient room conditions for about one week. The dynamic water-resistance was measured by the Dow Corning Leather Tester (14). The number of flexes to failure, i.e., flexes to initial water penetration, as determined by an electronic end point, was taken as a measure of the water-resistance. The data are given in Tables II and III.

RESULTS AND DISCUSSION

An attractive feature of the von Fuchs' lubrication process is the use of a small amount of lubricant, which meets one of the requirements of a substrate suitable for a water-repellent treatment, i.e., a low oil content in the fiber. This latter property suggested the use of ASA as a lubricant for leathers to be given water-repellent treatments in general, whereas von Fuchs limited his study to only one water-repellent treatment, namely ASA. This report is limited to a study of glutaraldehyde retanned chrome sides because previous work at our laboratory clearly indicated that a glutaraldehyde retannage of chrome leather, as well as lubrication with ASA, were factors that improved the efficiency (16). It should be pointed out that the treatments were on small pieces (4″ x 4″) on a laboratory scale since we were interested in the relative intraside comparison of three water-repellents; namely, silicone, Scotchgard, and Quilon, when used with the novel lubrication procedure of von Fuchs.

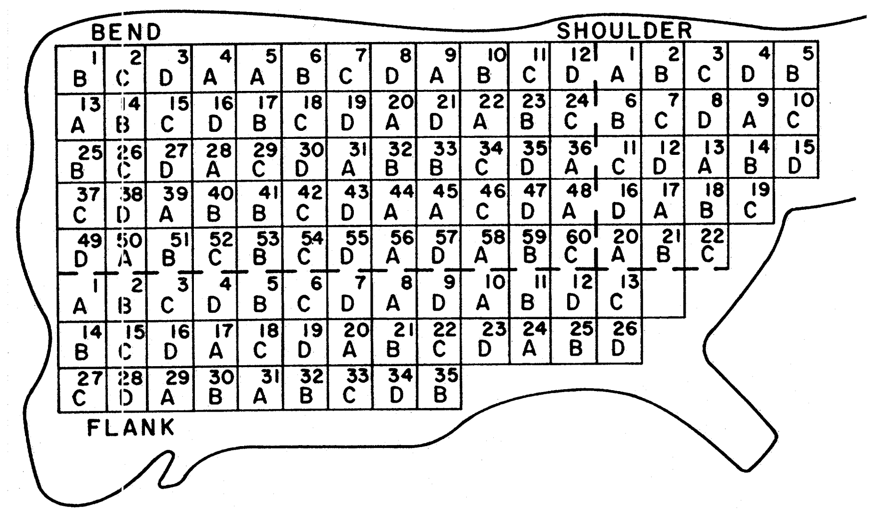

FIGURE 1.—Sampling positions for water-repellent treatments on Side T after dip lubrication by alkenyl succinic acid in tetrahydrofurfuryl alcohol and water.

The design used for sampling each side is indicated in Figures 1 and 2. This sampling method is referred to as stratification and it allows independent handling of separate strata relative to their importance, variation, number of samples, etc. (17). The samples received no finish treatments after lubrication and impregnation with water-repellent materials.

The variation in pickup of water-repellent substance by the various strata is indicated in Table I. As expected, the flank area had a higher content of water-repellent material than the bend or shoulder areas. The range or spread in values for pickup varied from about 15 to 30 percent of the average uptake value. This, of course, is one of the possible sources of variation in the data on flex values.

The individual data on water-resistance of the treated samples is given in Tables II and III. The position of the specimen in the side is designated in Figures 1 and 2. An arbitrary value of 86,400 flexes in the Dow Corning Leather Tester, which represents 24 hours of flexing, was selected as a cutoff point for leathers showing a high degree of water-resistance, i.e., values exceeding 86,400

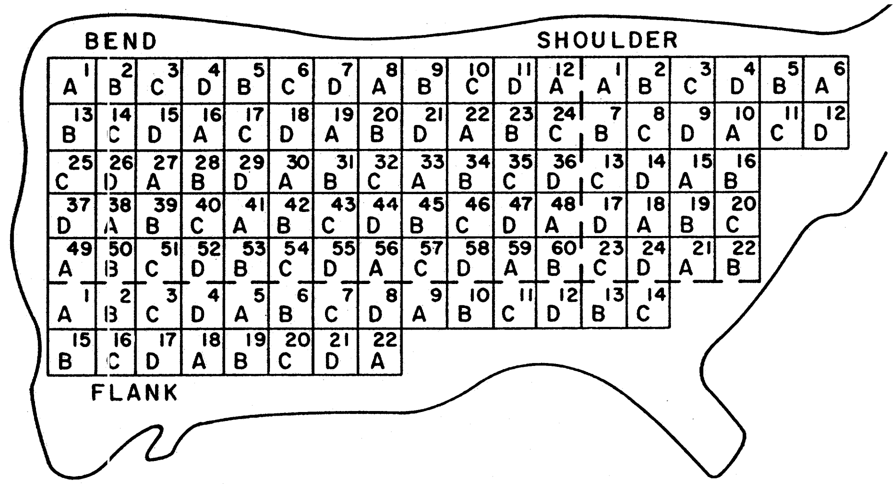

FIGURE 2.—Sampling positions for water-repellent treatments on Side M after dip lubrication by alkenyl succinic acid in mineral spirits.

TABLE I

AVERAGE UPTAKE OF WATER-REPELLENTS

	Treatment	Side M* Average Uptake Bend %	Shoulder %	Flank %	Spread	Side T† Average Uptake Bend %	Shoulder %	Flank %	Spread
A	Scotchgard FC-146	4.8	5.1	5.5	0.7	4.6	4.8	5.4	0.8
B	Quilon M	5.2	5.7	6.6	1.4	4.8	5.2	5.9	1.1
C	Silicone (low)	6.0	6.8	8.0	2.0	6.0	6.3	7.2	1.2
D	Silicone (high)	9.8	12.5	12.7	2.9	9.9	10.1	11.1	1.2

*Lubricated with ASA in Mineral Spirits, uptake 0.8% ASA.
†Lubricated with ASA in tetrahydrofurfuryl alcohol-water solution, uptake 1.0% ASA.

flexes to initial water penetration. It was felt that this upper limit was large enough to establish the relative worth of the treatments and served to expedite the testing of many samples as well. The high variability of the data is evident from the flex values in Tables II and III. In spite of the variability of the data, evaluation should not necessarily be a problem if we examine the fraction of the data exceeding an acceptable value. In fact, it is common practice in the industry to specify an arbitrary number of flexes, based on a particular test, as an indication of a satisfactory water-resistant leather (15).

TABLE II

FLEX VALUES* OF SAMPLES LUBRICATED WITH ALKENYL SUCCINIC ACID IN TETRAHYDROFURFURYL ALCOHOL-WATER (SIDE T)

Bend		Shoulder		Flank	
Position	Flexes	Position	Flexes	Position	Flexes
		A. Scotchgard, Uptake 4.9%			
4	38317	1	>86400	1	20180
5	>86400	9	>86400	8	>86400
9	>86400	13	>86400	10	>86400
28	41120	17	>86400	17	86365
31	41554	20	>86400	20	75885
36	>86400			24	67020
50	21850			29	28060
56	78790			31	>86400
58	50670				
		B. Quilon, Uptake 5.2%			
1	4020	2	10360	2	4980
6	11980	6	5020	5	9810
10	24340	14	19775	11	15490
25	9807	18	10270	14	27440
32	13240	21	12470	21	9430
33	7290			25	5480
51	5940			30	10520
53	20810			32	6510
59	6710				
		C. Silicone, Uptake 6.4%			
2	4390	3	32400	3	>86400
7	30080	7	21640	6	10430
11	65610	11	37270	13	>86400
26	12820	19	57290	15	>86400
29	>86400	22	41840	18	>86400
34	>86400			22	78170
52	>86400			27	>86400
54	>86400			33	>86400
60	>86400				
		D. Silicone, Uptake 10.3%			
8	>86400	4	>86400	4	>86400
12	>86400	8	>86400	7	>86400
16	7045	12	>86400	9	>86400
27	>86400	15	>86400	16	>86400
30	>86400	16	>86400	19	>86400
35	>86400			23	>86400
49	>86400			28	>86400
55	>86400			34	>86400
57	>86400				

*Flex values obtained from Dow-Corning Leather Tester.

TABLE III

FLEX VALUES* OF SAMPLES LUBRICATED WITH ALKENYL SUCCINIC ACID IN MINERAL SPIRITS (SIDE M)

Bend		Shoulder		Flank	
Position	Flexes	Position	Flexes	Position	Flexes
		A. Scotchgard, Uptake 5.0%			
1	>86400	1	>86400	1	>86400
8	84420	10	>86400	5	82960
12	6290	15	54950	9	>86400
27	>86400	18	28000	18	>86400
30	>86400	21	>86400	22	55290
33	46035				
49	>86400				
56	>86400				
59	44450				
		B. Quilon, Uptake 5.5%			
2	>86400	2	42460	2	12510
9	35420	6	36470	6	77890
20	67360	7	8900	10	22240
28	67320	19	21310	15	5910
31	63830	22	>86400	19	73660
34	40490				
50	>86400				
53	75160				
60	27040				
		C. Silicone, Uptake 6.6%			
3	11400	3	43740	3	39650
6	45830	8	22550	7	>86400
10	3610	13	35710	11	>86400
25	75040	20	>86400	16	73780
32	86170	23	>86400	20	>86400
35	>86400				
51	8260				
54	>86400				
57	>86400				
		D. Silicone, Uptake 10.8%			
4	>86400	4	3820	4	>86400
7	>86400	9	>86400	8	>86400
21	>86400	14	>86400	12	>86400
26	>86400	17	>86400	17	>86400
29	>86400	24	>86400	21	>86400
36	>86400				
52	>86400				
55	>86400				
58	>86400				

*Flex values obtained from Dow-Corning Leather Tester.

To aid in interpreting the data in Tables II and III therefore, this data is presented in the form of histograms as shown in Figures 3 and 4. These histograms are flex value distributions obtained for the various water-repellent treatments. Figure 3 shows the distribution of flex values for the three water-repellent treatments applied to the side lubricated with ASA in mineral spirits. From the distribution, the high level of silicone (10.8 percent) gave the highest degree of water-resistance. The Scotchgard (5 percent) and low level silicone (6.6

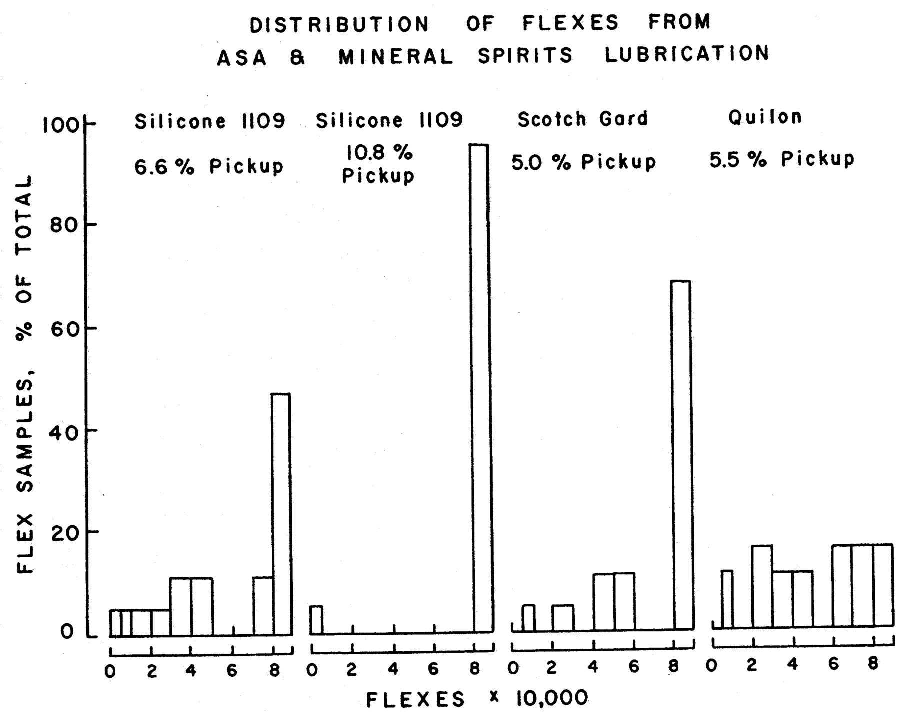

FIGURE 3.—Distribution of flexes from Side M. Those flex values terminated in the 80,000 to 90,000 range (>86,400) were included with those that failed in this range.

percent) were about comparable and Quilon (5.5 percent) was comparatively less efficient. For silicone and Scotchgard the distribution of flexes to initial water penetration was quite similar for the two methods of dip lubrication, i.e., ASA in mineral spirits (von Fuchs' procedure) or ASA in aqueous THFA. In the case of Quilon, much better results with respect to water-resistance were obtained with the side dip-lubricated by ASA in mineral spirits.

For unfinished leather, a value of 20,000 flexes to initial water penetration has been suggested as a reference point for adequate water-resistance.** From Figure 3, or Table III (lubrication with ASA in mineral spirits), it is apparent

**Acceptable level for unfinished leather suggested by a reviewer.

that 95 percent of the specimens with the high level of silicone (10.8 percent) or with Scotchgard (5 percent) showed flex values above 20,000. In the case of the lower level of silicone (6.6 percent) and Quilon (5.5 percent), the proportions of specimens exceeding this value were 85 and 84 percent respectively. From this standpoint, all of the treatments would appear promising for a good water-resistant leather.

Examination of the data in Figure 4 or Table II (lubrication with ASA in aqueous tetrahydrofurfuryl alcohol), from the same viewpoint regarding values above 20,000 flexes, gave similar conclusions except for Quilon. The proportions of specimens exceeding 20,000 flexes were 100 percent for Scotchgard; 95 percent for high-level silicone; 86 percent for low-level silicone; and only 14 percent for Quilon.

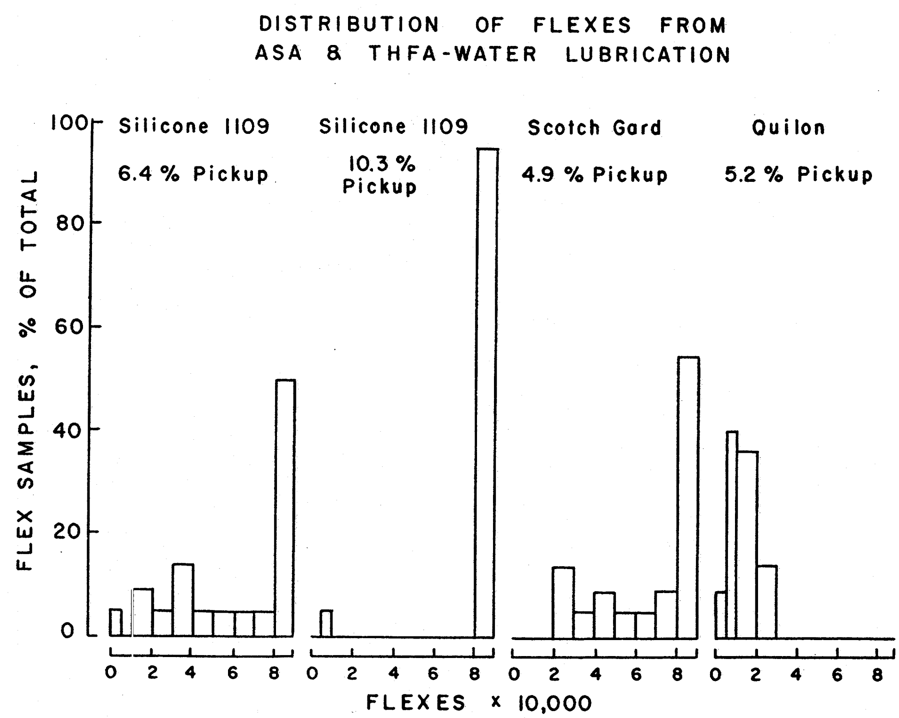

FIGURE 4.—Distribution of flexes from Side T. Those flex values terminated in the 80,000 to 90,000 range (>86,400) were included with those that failed in this range.

From the above evaluation of the data, lubrication by ASA in mineral spirits solution is more attractive than aqueous tetrahydrofurfuryl alcohol solution both from the viewpoint of low cost of solvent and water-resistance of the leathers.

An analysis of variance was made to compare the different water-repellent treatments within each side, i.e., one lubricated with ASA in mineral spirits; the other in aqueous tetrahydrofurfuryl alcohol. Table IV lists the flex averages to initial water penetration in order of decreasing magnitude for each of the lubricating systems and also the results of an analysis of variance, using Duncan's Multiple Range Test (18). Both sides ranked the treatments similarly. The "greater than" sign to the left of most of the averages indicates that these flex averages were weighted on the low side because the samples were not allowed to flex beyond 86,400. The vertical lines to the right of the averages establish the significance of the averages and bracket those averages which were, by statistical analysis, not significantly different.

TABLE IV

STATISTICAL ANALYSIS OF DATA FROM VARIOUS WATER-REPELLENT TREATMENTS

Treatment	Average Flexes to Initial Water Penetration*	
	ASA Lubrication, Mineral Spirits	ASA Lubrication, Aqueous THFA
D. High Silicone, Uptake Range 10.3–10.8%	>82053	>82792
A. Scotchgard, Uptake Range 4.9–5.0%	>71199	>68189
C. Low Silicone, Uptake Range 6.4–6.6%	>59841	>61016
B. Quilon, Uptake Range 5.2–5.5%	>49324	11435

*ASA stands for Casyl 18, an alkenyl succinic acid, and THFA stands for tetrahydrofurfuryl alcohol.

In the case of the mineral spirits lubrication system, treatment with high-level silicone and Scotchgard were not significantly different. The high-level silicone was, however, significantly different from the low-level silicone and Quilon treatments. The Scotchgard treatment was not significantly different from the low-level silicone treatment but was significantly different from the Quilon treatment. There was no significant difference between the low-level silicone and the Quilon treatments.

In the case of the aqueous tetrahydrofurfuryl alcohol lubrication system, the high-level silicone was significantly better than all of the other treatments. The Scotchgard treatment was not significantly different from the low-level silicone, but both were significantly larger than the Quilon treatment.

The statistical analysis discussed above was made on data from all three strata, i.e., bend, shoulder, and flank. A similar relative ranking of these treatments was obtained from data on samples taken only from the bend area.

SUMMARY

Chrome-tanned side leather in the blue was retanned with glutaraldehyde and lubricated by a dipping procedure with Casyl 18, an alkenyl succinic acid. This substrate was treated with various water-repellent agents, i.e., silicone, Scotchgard, and Quilon. The water-resistance of the treated leathers was evaluated by a dynamic test. In general, retannage with glutaraldehyde and lubrication with alkenyl succinic acid gave a leather substrate more efficiently treated with water-repellents. Of the four treatments studied, silicone at a level of about 10.5 percent in the leather gave the most water-resistant leather. Silicone at the 6.5 percent level and Scotchgard at the five percent level were about comparable to each other in effectiveness but somewhat less effective than the higher-level silicone. Quilon, at the five percent level in the leather was comparatively less efficient than silicone or Scotchgard. All three water-repellent agents, however, imparted an acceptable degree of water-resistance to this leather substrate.

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